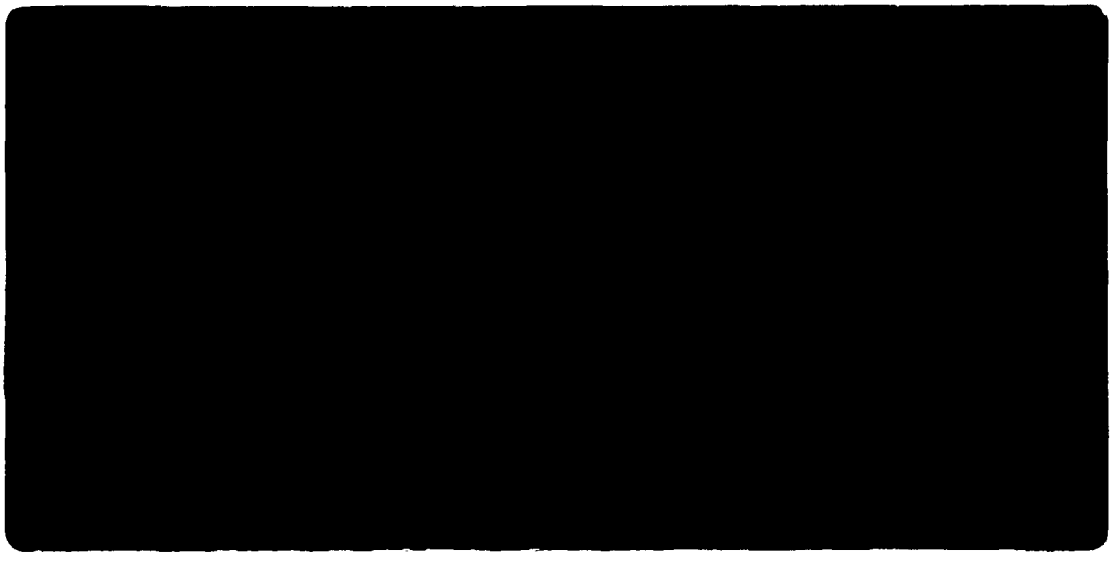
Institute of Paper Science and Technology
Atlanta, Georgia

IPST TECHNICAL PAPER SERIES



NUMBER 419

SIZING, AN OVERVIEW

B.W. CROUSE

JANUARY 1992

Sizing, An Overview

B.W. Crouse

Submitted to
1992 TAPPI Sizing Short Course
April 8–10, 1992
Nashville, TN

"SIZING, AN OVERVIEW"

B.W. CROUSE
DIRECTOR
RESEARCH SERVICES DIVISION
INSTITUTE OF PAPER SCIENCE
AND TECHNOLOGY
ATLANTA, GA
USA

PREPARED FOR THE
1992 TAPPI SIZING SHORT COURSE
APRIL 8-10, 1992
NASHVILLE, TN

ABSTRACT

The science of sizing is discussed in terms of wetting, surface tension and surface free energy. The penetration of liquids into paper and sizing against them are also discussed. Measures of sizing are reviewed relative to the significance of wetting rate.

KEY WORDS

Sizing, wetting, surface energy, liquid penetration, contact angle.

BACKGROUND

Surface and colloid chemistry are the two areas of physical science most closely associated with sizing and the sizing phenomenon. It has been stated that the objective of the sizing process is to make hydrophilic cellulose hydrophobic or lyophobic (1,2). If sizing is a major component of the field of paper chemistry, why does it have such a foreign name? Where did this term "sizing" come from?

A little lexicology will be instructive. The process of rendering hydrophilic cellulose hydrophobic requires the addition of something to cellulose to alter its response to liquids. To achieve this effect, some additives must be chemically attached or "fixed" to the cellulose surface. The French word "sise" means to set or fix. An early need for "setting" or "fixing" cellulose was to make it more suitable for gilding or painting (3). Since the Nineteenth Century the term has been extended to include the use of glue, starch, etc., to fill the pores of cloth and paper (4). In 1807 Morris Illig introduced internal sizing with rosin soap and alum as an alternative to animal glue (5). Today an extensive array of chemical additives are available for the papermaker to choose from. (Table 1).

WHAT IS WETTING?

We just said the objective of sizing was to make cellulose hydrophobic or nonwetting. What is wetting? Wetting is said to occur if the liquid:solid adhesion is greater than the liquid cohesion (1). In the simplest case that might be when the water: cellulose adhesion is greater than the water cohesion.

What does wetting look like? One way of visualizing and measuring wetting, or the lack of it, is by contact angle. Figure 1 shows two contact angles, both identified by θ. One shows an obtuse contact angle of 120° and the second an acute contact angle of 60°. When the liquid:solid adhesion is greater than the liquid cohesion wetting occurs. When this happens θ becomes $<90°$. When nonwetting occurs θ is $> 90°$ and for some hydrophilic surfaces it may be greater than 120° as seen in the "ducks back" effect with the common silicon compounds. With paper it is generally the rate of wetting that is of interest, more so than the equilibrium wetting.

What makes a surface wet? A few familiar terms are useful here. Surface tension of the penetrant is the inward attraction of the surface molecules in a bulk liquid which makes the air/liquid surface behave as if it were under tension. The surface tension of air/water at 20°C is 72.8mN/m while that of air/mercury at 20°C is 435.5 mN/m and air/acetic acid is 27.6 mN/m (6).

Therefore the choice of liquid or penetrant, to wet cellulose will have a bearing on the result (Table 2). Water might do a better job than mercury while acetic acid would do better yet. Specific free surface energy is the work necessary to increase the area of the surface isothermally and reversibly by a unit amount (7). Surfactants, or surface-active agents, are substances that when dissolved in another liquid reduce the surface tension between it and the other liquid and in so doing lower the specific free surface energy of the altered liquid. A good sizing agent would be one which would have a low specific free surface energy such that it would resist the tendency to "wet".

The short-range intermolecular forces which influence surface tension are van der Waals forces and hydrogen bonding (7). Hydrogen bonding is a contributing factor to the high surface tension of water. These forces are additive so the surface tension of water, γ_w, is the sum of the dispersion forces, γ^d_w and the hydrogen bonding, γ^h_w.

$$\gamma_w = \gamma^d_w + \gamma^h_w$$

or

$$72.8 \text{ mN/m} = 21.8 \text{ mN/m} + 51.0 \text{ mN/m}$$

At equilibrium, Young's equation may be used to explain the balance of surface forces (7). (Table 3). $\text{Cos}\,\theta = (\gamma sg - \gamma sl)/\gamma lg$

Where:

$\text{Cos}\,\theta$ = contact angle
γsg = surface energy of solid/gas interface
γsl = surface energy of solid/liquid interface
γlg = surface energy of liquid/gas interface

If the system is truly at equilibrium there is no increase in surface free energy and $\gamma sl + \gamma lg\text{Cos}\theta - \gamma sg = 0$

HOW DO LIQUIDS PENETRATE PAPER?

The much quoted Lucas-Washburn equation provides one view of the factors which influence the rate of liquid penetration into porous structures. In one version the equation takes the following form:

$$dl/dt = (\gamma/N)(r/l)\text{Cos}\,\theta$$

dl/dt = the rate of penetration due to capillarity
γ = surface tension of the penetrant
N = viscosity of the penetrant
r = capillary radius of an idealized porous substrate
l = depth of liquid penetration
θ = contact angle

This idealized expression for liquid flow in a uniform capillary illustrates that surface tension, a factor in the numerator and contact angle have a significant influence on the rate of cellulose wetting. Low-surface energy nonpolar solvents wet cellulose more rapidly than polar aqueous penetrants. The quantity (γ/N) is entirely controlled by the nature of the penetrant while the quantity (r/l) is controlled by the physical properties of the paper. The contact angle, θ, reduces the rate expression as it increases. This expression emphasizes that sizing is a temporary, time-dependent condition and it is the rate regulation which is most important (8).

Papermaking factors which influence the terms of the Lucas-Washburn equation include the dose and chemical nature of the internal and surface size compounds (θ) and the porous structure of the paper as influenced by its basis weight, porosity, density and moisture content (r/l). Sizing agents which provide the fiber with a low surface energy enable high-energy aqueous penetrants to form high contact angles. The higher the contact angle between the penetrant and the paper, the less freedom the penetrant has to move over or within the paper (9).

HOW DO YOU SIZE CELLULOSE?

One very effective way of sizing cellulose is to substitute all of the hydrophilic hydroxyl and carboxyl groups with something completely unreactive with water such as acetyl (Fig. 2). Such a modified cellulose is so well "sized" it no longer has the hydrogen bonding potential and becomes difficult to make into paper. More commonly accepted methods of sizing reduce some, but not all of the water reactive sites thus preserving some of the hydrogen bonding capacity and papermaking characteristics commonly associated with cellulose. An activated sizing complex is composed of a modular unit consisting of a hydrophobic group and a group reactive to cellulose. The water-resistant functionality must be made substantive to cellulose with the reactive group before sizing protection is imparted to the cellulose. The hydrophobic group is chemically bonded to cellulose at an end group or hydroxyl site. The cellulose then becomes less wettable since some of the hydrophilic sites are now occupied by a nonwetting functionality. Adjacent hydrophilic sites may be provided varying degrees of protection by two factors: (1) the physical coverage provided by the hydrophobic polymer configuration and (2) the specific surface chemistry of the hydrophobic group.

WHAT ARE SOME SIZES FOR CELLULOSE?

Table 1 lists a few of the sizing materials in use today. During the balance of this course you will receive detailed information on many of the principal sizes listed here. Table 4 takes six of the more common sizes and identifies not only the size complex but also its cellulose reactive group and its liquid resistant functionality.

Most molecular diagrams depicting sized paper do not show the entire structures because they become to unwieldy. Just to illustrate the point, Figure 3 attempts to show a cellobiose dimer with one functional group replaced with an alkylketene dimer unit.

HOW DO YOU MEASURE SIZING?

As we have discussed earlier, a sized paper resists wetting so one measure might be the contact angle itself. The actual measurement of sizing is perhaps one of the most difficult aspects of sizing technology. It isn't that the measurement process itself is inherently difficult but the selection of a size test procedure, penetrant and test conditions that accurately reflect the desired end-use performance can be a challenge. In some cases even after we have selected an appropriate sizing test, penetrant and test conditions, a single number may not reveal the true story if it is the wetting rate that is of interest. In this case a series of numbers over time may be more useful than an individual result.

In the first offering of this course 12 years ago Jerome Gess gave an excellent review of the measurement of sizing which was then published in Tappi (10). More recently Klumer has also addressed the subject (2). There is no universal method for determining the degree to which a paper is sized. Before attempting to make such a measurement you must ask yourself how the paper product will be used and what test procedure will best simulate the actual end use conditions. You must then ask yourself what is the best choice of penetrant, penetrant and specimen temperature and specimen moisture content. Finally you must select a time interval that will illustrate the rate effect over the appropriate period.

REFERENCES

1. Swanson, J.W., (ed.), "Internal Sizing of Paper and Paperboard," TAPPI Monograph Series No. 33, TAPPI Press, 1971.

2. Reynolds, W.F., (ed.), "The Sizing of Paper," second ed., TAPPI Press, 1989.

3. The Oxford English Dictionary, Second Ed., 1989, Clarendon Press, Oxford, England.

4. The Random House Dictionary of the English Language, 1966, Random House, NY.

5. Casey, J.P., "The Manufacture of Pulp and Paper," 3rd Ed., Vol. 4, Chapter 5, p. 2, 1938, McGraw-Hill, NY.

6. Weast, R.C., (ed.), "Handbook of Chemistry and Physics," 48th Ed., 1967, The Chemical Rubber Co., Cleveland, OH.

7. Shaw, D.J., "Introduction to Colloid and Surface Chemistry," 3rd Ed., Butterworths, 1980, London, England.

8. Griggs, W.H., Crouse, B.W., "Wet end sizing- an overview," TAPPI, 63 (6), June 1980, p. 49-54.

9. Davidson, R.W., TAPPI, 58 (3), 1975, p. 48.

10. Gess, J.W., "The measurement of sizing in paper," TAPPI 64 (1), January 1981, p. 35.

Table 1

Paper Sizes

1. Alkenyl succinic anhydride (ASA)
2. Alkylketene dimer (AKD)
3. Aluminum stearate
4. Copolyester
5. Dispersed rosin
6. Fluorchemicals
7. Fortified rosin
8. Gelatin
9. Latexes
10. Polyurethane
11. Rosin soap
12. Silanes, silicates
13. Starch
14. Stearto chromic chloride
15. Styrene maletic anhydride (SMA)
16. Wax emulsions

Table 2

Common Paper Penetrants

1. ink
2. milk
3. citrus juices
4. hot drinks
5. cold drinks
6. oils
7. greases
8. blood
9. organic solvents
10. water
11. toners

Table 3

Young's Equation

(balance of surface forces)

- Cos θ = (Gsg - Gsl)/Glg
- Gsg = surface energy, solid/gas interface
- Gsl = surface energy, solid/liquid interface
- Glg = surface energy, liquid/gas interface

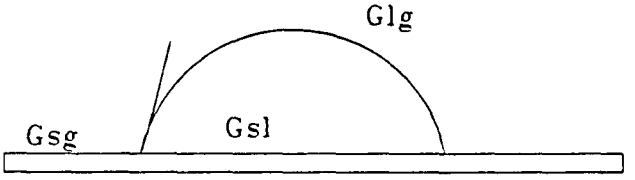
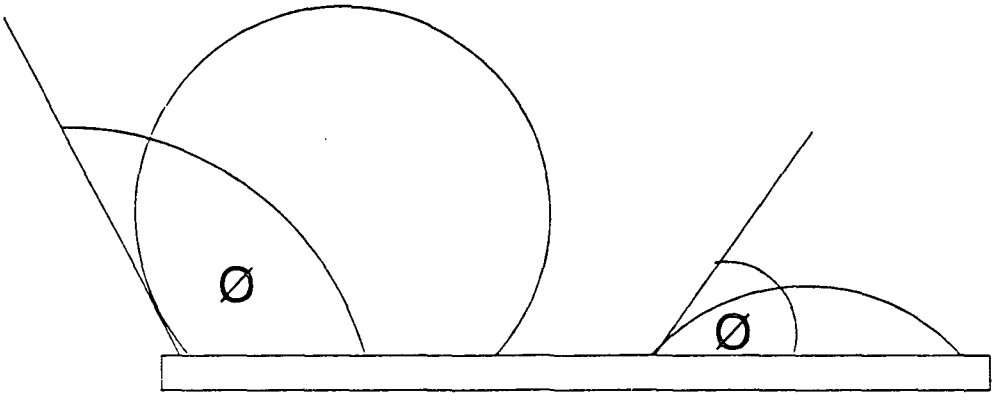


Table 4
Common Cellulose Sizes

Size Complex Functionality	Cellulose Reactive Group	Liquid Resistant Functionality
Aluminum resinate	Acid sulfate or acid chloride	Abietic acid (rosin)
Alumimum stearate	Acid sulfate or acid chloride	Stearic acid
Distearic-anhydride	Anhydride	Stearic acid
Alkenyl succinic anhydride	Anhydride	Alkylated succinic acid
Styrene maleic anhydride	Anhydride	Styrene copolymer
Alkylketene dimer	Alkylated ketene	Stearic acid

Figure 1

Contact Angle & Wetting



t1 t2

Figure 2

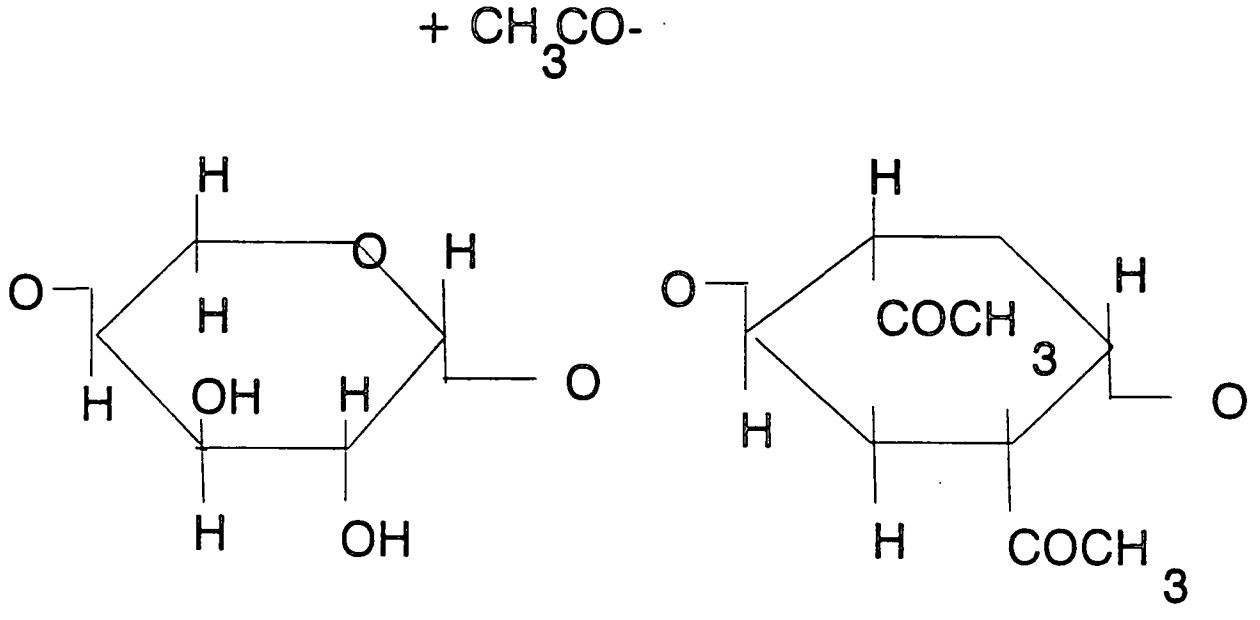


Figure 3